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TREATMENT METHOD FOR STORING TUNA

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Specification

1. Title of the invention

Treatment Method for Storing Tuna

2. Claims

1. A treatment method for storing a tuna, characterized by the fact that in a smoke treatment by contacting a smoke containing a CO gas generated by smoking a smoking material with a fresh tuna meat being treated, a number of smoke injection needles arranged in parallel are pierced through the tuna meat; bubbles of the above-mentioned smoke are dispersedly injected into the tuna meat by inserting or extracting the smoke injection needles while intermittently repeating a small amount of bubble-shaped spray of the above-mentioned smoke from said injection needles; thereby, the residual CO concentration in the tuna meat is controlled to 1,500-2,400 μg/kg; and the tuna meat treated in this manner is frozen and stored in the vicinity of -18°C.

[1] Numbers in the margin indicate pagination in the foreign text.

2. The treatment method for storing a tuna of Claim 1, characterized by the fact that the browning suppression period during freezing in the vicinity of -18°C is 2.5-3.5 months; and browning of the smoked tuna meat after thawing is almost similar to browning of an untreated tuna meat.

3. The treatment method for storing a tuna of Claim 1 or 2, characterized by the fact that the smoke is injected into the tuna meat through the smoke injection needles.

4. The treatment method for storing a tuna of any of Claims 1-3, characterized by the fact that as the measured value of the residual CO concentration in the tuna meat, the CO coordinated with a myoglobin in said tuna meat is removed by heating the tuna meat while blowing a pickup gas into a fixed amount of boiled water and dissipated into the pickup gas; these gases are housed in a tetra bag; and the gas concentration in said back is measured by a detecting pipe or gas chromatography.

3. Detailed explanation of the invention /2

[0001]

(Technical field of the invention)

The present invention pertains to a method for appropriately storing a tuna for eating in a raw state being used as a sliced raw fish or sushi rice.

[0002]

(Prior art)

The red pigment of fish meats is mainly a pigment containing a heme iron such as myoglobin (Mb) and hemoglobin (Hb). It is said that the tuna is a representative lean meat fish, and 90% of a heme iron pigment in an ordinary tuna meat and 80% or more in a blood and meat are Mb. The inside of a fresh tuner meat exhibits a red purple color, and at that time, the Mb is a substitutional Mb containing divalent iron ions. If it is exposed into an air, it is coupled with oxygen (O_2) in the air and changed to a scarlet oxymyoglobin (O_2Mb). However, it is held for a long time in the air, the iron coupled with the Mb is oxidized from divalent iron to trivalent iron, so that a brown Met myoglobin (MetMb) (it is called Met processing or browning). However, the browning is advanced, even without being exposed to the air. Also, the higher the temperature, the faster the browning progress. In order to suppress the browning, currently, the tuner is frozen and stored at a very low temperature of -60°C or lower or treated with CO or subjected to a pH adjusting method. The tuner in a scarlet O_2Mb state is fresh and has a product value, and the tuna in which a brown Met myoglobin (MetMb) is generated looks dirty and has no product value.

[0003]

In order to prevent the browning and to hold the meat color, a very low temperature of -60°C is currently adopted for freezing the tuner for a sliced raw fish. The reason why freezing at a very low temperature of -60°C or lower is adopted although the degradation or change of each component in the tuner meat is sufficiently suppressed by freezing at -18°C (temperature of a freezing chamber of a home refrigerator) is that the Met processing (browning) is not suppressed during freezing at -18°C and the product value as a sliced raw fish disappears. However, the decrease of the freshness and the browning are not necessarily coincident with each other.

Also, since a very low-temperature freezing facility of -60°C is used only in Japan and the freezing facility of -60°C is not general in foreign countries, the tuna frozen at -60°C /3 cannot be essentially used and processed.

[0004]

As the method for preventing the browning other than the very low-temperature freezing of -60°C or lower, there is a CO gas (chemically synthesized 100% CO gas) treatment. However, in the CO treatment, the color of the tuna meat is a natural color tone but is changed to an excessively fresh pink system color tone (an unnatural fresh color), so that the change of the color

being caused by the decomposition of the tuna meat is covered and concealed. Thereby, a low-grade tuna with poor qualities is made to appear as a high-grade product, and a deceptive processing for giving consumer a wrong impression about the freshness. This deceptive processing is reliably achieved by a treatment using a chemically synthesized 100% CO gas.

Furthermore, it is characterized by the fact that the color is not changed for 1-2 years during freezing at -18°C and a fresh color is. If the tuna was stored in a home refrigerator, the color was not changed for several months, and consumers make a mistake in judging the freshness.

As one method that prevents the browning of a tuna meat and hold the meat color, currently, there is a pH adjustment. In this method, similarly to the CO gas-treated tuna, the color tone of the tuna which is prevented from being browned by the pH adjustment continuously holds a fresh color tone over a long term, and browning is not caused for about one week after thawing (in a raw state), like a natural untreated tuna, so that consumers are likely to fail to recognize the freshness.

[0005]

On the other hand, in Japanese Kokai Patent Application No. Hei 6[1994]-292503, these inventors previously proposed that the qualities of a tuna meat for eating in a raw state being used as

a sliced raw fish or sushi rice could be maintained for a long time by a low-temperature smoke treatment.

In the above-mentioned previously proposed is totally different from the method for improving the storage of foods by the conventional smoke treatment (smoking), the browning is prevented by a quality maintenance treatment using a low-temperature smoke in the range where the sense of food, flavor, smell, etc. of the tuna for eating in a raw state can be sufficiently responded to eating in a raw state of sliced raw fishes without being particularly different from those of the conventional tuna for eating in a raw state.

[0006]

In the above-mentioned method for smoking a tuna meat for eating in a raw state proposed by these inventors, a smoke is generated by smoking, unnecessary smells and tar portion are /4 filtered by passing it through a filter. Then, the smoke is brought into contact with a raw tuna meat and smoke-treated.

However, in this method, for thick cut meats for a high-efficient treatment of the tuna meat, the permeation of the smoke into the surface layer is relatively fast. However, a long time is required for the smoke to sufficiently permeate into the inside, and the freshness of the tuna meat is lowered in the meantime.

[0007]

For the relationship between the permeation depth of the CO gas in the tuna meat and the time, these inventors obtain the measurement results of the permeation of 5 mm after 1 h, 9.5 mm after 6 h, 20 mm after 30 h, and 25 mm after 48 h when the smoke is permeated into a tuna meat with good freshness from the outer surface of the tuna meat by contacting. In other words, in case the CO gas is brought contact with the outer surface (both the upper and lower surfaces) of the tuna meat with a thickness of 50 mm, 48 h is required for the CO gas to be completely permeates into the central part, and in the meantime, the freshness decrease and the decrease of the sense of taste and the appetite due to the drip outflow cannot be avoided.

A lower temperature of the tuna meat being treated is preferable in terms of maintenance of the freshness (for example, 1-3°C), however the permeation of the smoke into the tuna meat being treated is decreased with the decrease of the temperature.

The above-mentioned relationship between the permeation depth and the time is obtained at a temperature of 1-3°C, and the permeation depth is further increased with the further increase of the temperature.

If the freshness is slightly inferior and the meat quality is poor, the smoke is not permeated into the central part unless a large amount of time is applied. It is also similar to the above-mentioned case where the chemically synthesized 100% CO gas is brought into contact with a raw tuna. Also, in this case, the tuna is a yellowfin tuna.

[0008]

In order to improve this problem, in Japanese Kokai Patent Application No. Hei 8[1996]-168337, these inventors already proposed a high-efficient treatment method for storing a tuna for eating in a raw state that pierces a number of smoke injection needles arranged parallel at a fixed interval into a tuna meat and uniformly and three-dimensionally injects smoke bubbles with a fixed pressure and a fixed volume into the tuna meat by extracting the smoke injection needless while intermittently repeating the bubble-shaped spray of the smoke into the tuna meat, so that a storage treatment is applied to the tuna meat. /5

[0009]

If the storage treatment of this method was applied, the browning was suppressed by freezing at a temperature of about -18°C (the temperature of the freezing chamber of a home refrigerator), even without using a very low-temperature

freezing of -60°C for a long-term storage of the tuna meat for eating in a raw state, however an appropriate amount of smoke treatment was always required in consideration of the CO concentration (background value) in an untreated tuna meat).

Accordingly, these inventors confirmed that if the above-mentioned appropriate amount of smoke was injected in consideration of the background value and the residual CO concentration in a tuna meat was set to a range of 1,500-2,400 μg/kg, the browning suppression period during freezing in the vicinity of -18°C was about 2.5-3.5 months required for circulation, an excessively fresh pink color was not formed after thawing, unlike a tuna treated with 100% CO gas, browning of the smoke-treated tuna after thawing was almost similar to browning of an untreated tuna meat, and the color tone was changed similarly to an untreated tuna, so that consumer could not make a mistake in judging the freshness.

[0010]

(Problems to be solved by the invention)

The present invention is based on such a knowledge, the technical purpose of the present invention is to provide a treatment method for storing a tuna that can sufficiently suppress the degradation and change of each component of a tuna meat, even at a freezing temperature in the vicinity of -18°C at

which a low facility cost and a small amount of energy are required, can maintain the qualities during freezing and transporting for a required period at the temperature, prevents browning of the tuna meat during said freezing, changes the color of the tuna meat similarly to the change of the color of an untreated tuna meat with time after thawing, and prevents consumers to make a mistake in judging the freshness, etc., due to an excessive storage treatment.

[0011]

(Means to solve the problems)

In order to achieve the above-mentioned purpose, the treatment method for storing a tuna of the present invention is characterized by the fact that in a smoke treatment by contacting a smoke containing a CO gas generated by smoking a smoking material with a fresh tuna meat being treated, a number of smoke injection needles arranged in parallel are pierced through the tuna meat; bubbles of the above-mentioned smoke are dispersedly injected into the tuna meat by inserting or extracting the smoke injection needles while intermittently /6 repeating a small amount of bubble-shaped spray of the above-mentioned smoke from said injection needles; thereby, the residual CO concentration in the tuna meat is controlled to 1,500-2,400 μg/kg (the value measured by the Kumazawa method

which will be mentioned later); and the tuna meat treated in this manner is frozen and stored in the vicinity of -18°C.

[0012]

In the above-mentioned treatment method for storing a tuna, it is effective to inject the smoke into the tuna meat through the smoke injection needles since th smoke treatment is carried out in a short time in which the freshness is not lowered.

Also, as the measured value of the residual CO concentration in the tuna meat, the CO coordinated with a myoglobin (Mb) in said tuna meat is removed by heating the tuna meat while blowing a pickup gas into a fixed amount of boiled water and dissipated into the pickup gas, these gases are housed in a tetra bag, and the gas concentration in said back is measured by a detecting pipe or gas chromatography.

[0013]

According to the above-mentioned treatment method for storing a tuna, the browning suppression period during freezing in the vicinity of -18°C is 2.5-3.5 months required for easy circulation, and browning of the smoked tuna meat after thawing is almost similar to browning of an untreated tuna meat. Thus, the tuna storage treatment in which consumers do not make a mistake in judging freshness, etc., is possible.

Here, it should be noted that the facility cost and the amount of energy required for freezing, storage, etc., at -18°C are much lower than the facility cost and the amount of energy required for super-freezing and storage at -60°C, and for this reason, according to the above-mentioned method, the cost for circulation can be considerably reduced.

Furthermore, if the disassembled tuna meat can be frozen at -18°C by such a smoke treatment, since only the edible portion is frozen, stored, and transported and the edible portion is about 35% on the average, freezing, storing, and transporting of about 65% dust (burnt part) can be excluded, compared with a very low-temperature freezing at -60°C and an air transport of fresh fishes. Thus, this treatment is also very favorable for economical efficiency and earth environment preservation (flon and CO_2 discharge suppression).

[0014]

/7

In the treatment method for storing a tuna of the present invention, while holding a tuna meat in a substantially raw state, antisepsis and sterilization effects are given by the utilization of a smoke, and the degradation and change of each component in the tuna meat can be sufficiently suppressed, even at a freezing temperature, so that the qualities can be maintained during freezing and transporting for circulation.

Furthermore, in the method of the present invention, the residual CO concentration being obtained from the relationship between the amount of smoke in the bubbles and the residual CO concentration (background value) in an untreated tuna is controlled to 1,500-2,400 μg/kg by injecting a necessary amount of smoke containing CO into the tuna meat by the injection needles. The smoke treatment in which the residual CO concentration is adjusted by the smoke injection needles is very effective for a smoke treatment up to the deep inside of the tuna meat in a short time without damaging the freshness of the tuna meat.

[0015]

Furthermore, regardless of the thickness of the tuna meat (fillet or loin), the residual CO concentration can be made uniform in a short time, and the browning period after thawing can be freely adjusted to 7 days or 9 days by adjusting the residual CO concentration. Thus, the storage treatment of the tuna meat with excellent qualities can be realized at a uniform residual CO concentration.

The relationship between the time and the depth of the permeation and diffusion of the smoke gas into the tuna meat is not a simple curve relationship mentioned in the above-mentioned section 0007. The precise and uniform coordination of the CO

gas being included in the smoke into the meat can be achieved only by the needle puncher.

[0016]

(Embodiments of the invention)

In the smoke treatment of a tuna meat by the method of the present invention, first, it is necessary to generate a smoke with desired components, and for this reason, a smoke is generated by a smoke generation mechanism as shown in Figure 1.

Said smoke generation mechanism 1 consists of a hopper 5 into which a wood chip being a smoking material in which size, moisture, kind, etc., are adjusted in advance are charged, a screw type transfer means 6 equipped with a heating means 7 which transfers the above-mentioned wood chip being supplied /8 from said hopper 5, a gas discharge tube 8 which is installed behind said screw type transfer means 6 and to which a high-pressure washing water is supplied, a gas-liquid separating tube 9 to which a gas discharged from said gas discharge tube is guided, a diaphragm pump 10 which transfers the smoke separated by said gas-liquid separating tube 9, a smoke filter (deodorizing tower) 11 connected to said diaphragm pump 10, and a control means (not shown in the figure) which controls the operation of these equipments and can control the transfer rate of the wood chip, the heating temperature of the heating means,

the amount of smoke flow being generated, and the CO concentration in the smoke.

[0017]

The above-mentioned screw type transfer means 6 has a cylindrical cylinder 15 being connected to the outlet of the above-mentioned hopper 5, a spiral screw 16 which is installed in said cylinder 15 and installed at a screw shaft 17 extending in its axial direction, and a screw motor 18 which is installed outside said cylinder 15, is connected to the above-mentioned screw shaft 17 through the cylinder 15, and drives the above-mentioned screw 16. The wood chip in the cylinder 15 is transferred by rotating the screw 16.

In the above-mentioned heating means 7, part of a circular tube constituting the above-mentioned cylinder 15 is covered with a large-diameter circular tube 20, whose both ends are closed, having a partition wall 20a in the diameter direction at the center, and a first heater 22 and a second heater 23 are arranged in each of two rooms 21a and 21b partitioned by the partition wall 20a formed between part of the circular tube constituting said cylinder 15 and the large-diameter circular tube 20. The wood chip being transferred into the cylinder 15 is heated by heating part of the circular tube constituting the

above-mentioned cylinder by said first heater 22 and second heater 23, so that a smoke is generated.

[0018]

The above-mentioned heating means is divided into two stages of the first heater 22 and the second heater 23, and heating of the first heater 22 of the former stage is a low-temperature heating (preheating) and is heating up to the temperature right before the thermal decomposition of the wood chip.

Heating of the second heater 23 of the latter stage causes a thermal decomposition in the presence of a very small amount of oxygen and generates a smoke.

Since the above-mentioned heating means 7 performs heating by dividing into two stages, the smoke components are stable, even if the water content of the raw materials is different.

In the rear part from the above-mentioned heating means 7/9 of the above-mentioned cylinder 15, the above-mentioned gas discharge tube 8 is installed, and the above-mentioned screw 16 is extended up to the inside of said gas discharge tube 8. A mixture of gas, liquid, and solid, which are generated when the wood chip is heated by the above-mentioned heating means 7, is transferred, and the water from a water storage tank 70 is sprayed as a high-pressure washing water via pump 71, pipe 72,

and opening and closing valves 73 and 74 to said gas discharge tube 8.

In the gas being transferred to the above-mentioned gas discharge tube 8, a large amount of carbon particles and a gas-state tar portion are included, however since the gas contact surface of said gas discharge tube 8 is washed with the high-pressure washing water by spraying the high-pressure washing water, the attachment of the carbon and tar to the contact surface is prevented.

[0019]

The above-mentioned screw shaft 17 has a structure in which it is cooled with the washing water, however if an appropriate cooling is not maintained, a gas leak is likely to be generated from a packing part installed at the tip of said screw shaft.

The mixture of gas, liquid, and solid transferred to the above-mentioned gas discharge tube 8 is separated into gas, liquid, and solid in said gas discharge tube 8, and the gas is guided to the gas-liquid separating tube 9 through a gas discharge pipe 81 in which a high-pressure washing water is sprayed via an opening and closing valve 75. The solid and the liquid are continuously dropped with the washing water to a discharged carbon receiving plate 83, overflowed from said discharged carbon receiving plate 83, and dropped onto a wire

net 84, the water is guided to the water storage tank 70, and the solid is guided to a discharged carbon storage 85.

The water of the water storage tank 70 is circulated as a high-pressure washing water, however if necessary, a supplemental water is supplied to the water storage tank 70.

The state of said smoke generation mechanism 1 can be indirectly detected by the discharged carbon state. For example, when the sintered particles of the discharge carbon are large, the wood has a large tar portion, and the gas generation is apt to be unstable. At that time, chaffs, activated carbon, etc., are sometimes mixed with the smoking material.

[0020]

The above-mentioned diaphragm pump 10 is connected to a pressure maintenance means 92 having a pressure detection means installed in the gas-liquid separating tube 9, and the smoke separated by the gas-liquid separating tube 9 is transferred at a fixed pressure.

The mixture ratio of the air in the smoke is relatively precisely controlled by setting the pressure in the pressure maintenance means 92. If the pressure in the gas discharge pipe 81 is set to a negative pressure, the air is absorbed by the hopper 5, and the smoke is diluted. /10

If the pressure in the gas discharge pipe 81 is set to a positive pressure, the mixture of the air from the hopper 5 is reduced, however if the pressure is set to a too high pressure, the smoke generated flows back to the hopper 5.

[0021]

Said smoke generation mechanism 1 is an external heating system, and its control is completely electrically carried out. However, the amount of smoke being generated is determined by the capacity of a heat source.

In said smoke generation mechanism 1, the amount of smoke flow being generated is in a range of 4-6 L/min, and it is difficult to generate a large amount of gas at a time. However, in case a large amount of smoke is required at a time, the smoke generated in advance is stored in a storage part such as bag and used in the smoke treatment.

As mentioned above, said smoke generation mechanism 1 has a feature in which the amount of smoke flow being generated can be adjusted and has a further feature in which the CO concentration of the smoke can also be adjusted.

Specifically, the CO concentration in the smoke is adjusted by the control of the heater temperature and the adjustment of the screw feed rate. Therefore, the smoke with a favorable CO concentration is steadily, stably, and reliably generated.

[0022]

As the smoking material being used in the above-mentioned smoke generation mechanism 1, various kinds of trees being used for a general smoking treatment can be used, and for example, evergreen oak, Japanese oak, Japanese beech, cherry tree, alder, Japanese linden, oak, walnut, Japanese chestnut, white birch, hickory, poplar, plane tree, etc., can be used.

[0023]

The smoke in which the above-mentioned smoke components and the CO concentration are adjusted to an appropriate amount is introduced into the smoke filter (deodorizing tower) 11, and the smoke generated is passed through the filter. Tar portion and smells are mainly removed from the smoke, and the smoke containing components having a high antisepsis, sterilization, and discoloration suppression effect is passed. As the filter for removing smells, activated carbon, etc., are appropriate.

[0024]

The smoke obtained in this manner is brought into contact with the tuner met being treated and smoke-treated, and in /11 the treatment, as will be explained below, smoke bubbles are three-dimensionally, uniformly dispersed into the tuna meat by using smoke injection needles.

First, at the outlet of the above-mentioned smoke filter 1, an absorber such as vacuum pump is connected via a pipe, and the smoke drawn out by the absorber is used to contact with the tuna meat for eating in a raw state in the next smoking treatment process.

Since the treatment is completed in a very short time in the smoking treatment process, using a cooled smoke is not particularly required.

[0025]

Also, the smoke drawn out by the above-mentioned absorber is housed in a gasbag such as vinyl bag or an appropriate container, and if necessary, it is stored and cooled in a refrigerator. The gas bag or container is connected to a smoke supply port of a smoke injector in the smoking treatment process, and the cooled smoke housed in it can also be brought into contact with the tuna meat for eating in a raw state.

[0026]

In the smoking treatment process, noticing from the past experimental examples that the degree of smoke permeation per 1 h at the initial stage into the tuna meat was 4 mm or more, a number of smoke injection needles 32, which are arranged in parallel at a nearly fixed interval (for example, an interval of several mm) in which the above-mentioned degree of permeation is

considered, are pierced into said tuna meat M, and the above-mentioned smoke is sprayed in a bubble shape at a fixed pressure and a fixed volume from its tips. While inserting or extracting the smoke injection needles 32, the spray is intermittently repeated at an interval of several mm, and a fixed amount of smoke is injected at a fixed interval, so that a small amount of bubbles of the smoke is dispersedly injected into the tuna meat and uniformly permeated and diffused into the tuna meat M from the inside.

[0027]

From the relationship between the CO concentration of the smoke and the background value of the CO concentration in an untreated tuna meat, the amount of smoke in the bubbles is set so that the final residual amount of CO may be included in a range of 1,500-2,400 μg/kg. This range was experimentally and experientially confirmed by these inventors as the range where the browning suppress period during freezing in the vicinity of -18°C for a tuna meat with good freshness was 2.5-3.5 months and browning of the smoked tuna meat after thawing was almost similar to browning of an untreated tuna meat. The amount of/12 CO being injected as a smoke can be optionally set by the adjustment of CO concentration in the smoke and the adjustment

of the smoke pressure, the amount being injected, the injection interval, etc.

[0028]

The browning of the tuna meat during freezing and storing at -18°C is suppressed mainly by the carbon monoxide (CO) of the smoke. In other words, the coordination of O_2 is considerably suppressed (the affinity of CO to the reducing Mb containing divalent iron ions is 100 times or more of O_2) by coupling (coordination) of CO with the reducing Mb containing divalent iron ions, so that the oxidation (browning) from the divalent iron to a trivalent iron is suppressed. The carbon monoxide concentration of the smoke is high: the higher the residual CO concentration of the tuna, the larger the browning suppression effect. For this reason, the browning suppression period of the tuna meat being held at -18°C is lengthened with the increase of the CO concentration of the smoke gas and the smoke treatment time. However, if the residual CO concentration is too high, since the treated tuna exhibits an unnatural scarlet color and the fresh red color is held over a long term after thawing (browning is not caused), it is necessary to set the residual CO concentration so that the browning suppression period during freezing at -18°C may be 2.5-3.5 months in consideration of the circulation of the frozen tuna.

[0029]

Along with the above-mentioned this smoke process, antisepsis, sterilization, and flavor improvement effects can be given only by an infinitesimal amount of components other than CO of the smoke.

There are about 200 kinds of organic compounds being included in said smoke, and the main organic compounds are shown in Table I.

[0030]

(Table I)

/13

Acid Formic acid Complex acid	 HCOOH CH_3COOH
Aliphatic aldehyde Formaldehyde Acetaldehyde	 HCHO CH_3CHO
Ring-shaped aldehyde Furfurol Methylfurfurol	 C_4H_8OCHO $CH_3C_4H_2OCHO$
Aromatic aldehyde Vanillin Silingicualdehyde	 $CH_3COC_6H_3(OH)CHO$ $(CH_3O)_2C_6H_2(OH)CHO$
Aliphatic ketone Acetone Methyl ethyl ketone	 CH_3COCH_3 $CH_3COCH_2CH_3$
Ring-shaped compound ketone Methyl alcohol Ethyl alcohol	 CH_3OH CH_3CH_2OH
Monovalent phenol Phenol Cresol Xylenol Anilnol Thyhil	 C_6H_6O C_7H_8O $C_8H_{10}O$ C_7H_8O $C_{10}H_{14}O$

Divalent phenol	
Pyrocatechine	$C_6H_8O_2$
Guwayacol	$C_7H_6O_2$
Ethyl guwayacol	$C_9H_{12}O_2$
Propyl guwayacol	$C_{10}H_{14}O_2$
Eugenol	$C_{10}H_{12}O_2$
Trivalent alcohol	
Pyrogallol	$C_6H_6O_3$
Monomethyl ether	$C_7H_8O_3$
Dimethyl ether	$C_{11}H_{16}O_3$
Veratrol	$C_8H_{10}O_3$
Base	
Methylamine	CH_3NH_2
Ethylamine	$C_2H_8NH_2$
Hydrocarbon	
3,4-benzpyrene	$C_{20}H_{12}$

[0031]

In the above-mentioned smoke injector 3, as shown in Figure 3, a number of injection needle supports 31 in which a number/14 of smoke injection needles 32 are arranged in parallel at a fixed interval are arranged so that each injection needle 31 may be positioned between the adjacent injection needles 32 in the adjacent injection needle supports 32, that is, the injection needles 32 may be different from each other. Thus, in the injector body 30 being constituted by the above-mentioned injection needle supports 31, several tens to several hundreds pieces of the above-mentioned injection needles 32 are regularly arranged in a number of rows and columns at a fixed interval, and the smoke is injected at a fixed interval into the tuna meat M into which the injection needles are inserted via through

holes in the smoke injection needles 32. In each injection needle support 31, a smoke supply pipe 33 for introducing the smoke sent through the above-mentioned smoke filter 11 or a smoke cooler or the smoke housed and stored in the gas bag such as vinyl bag is installed.

[0032]

In case the smoke from the above-mentioned filter 11 or smoke cooler is introduced, the smoke distributing pipe may be connected to the smoke supply pipe 33. In case the smoke housed and stored in the gas bag such as vinyl bag is introduced, the gas bag is made to be able to be attached and detached to and from the smoke supply pipe 33 and is sequentially exchanged when the smoke disappears, and the smoke can be supplied into the smoke injection needles 32.

If necessary, the smoke can be supplied after pressurizing it at about 2-10 kg/cm^2 by a pressurizer installed in the smoke supply pipe 33.

[0033]

In the above-mentioned each injection needle support 31, as shown in Figure 2, a movable valve 34 being constituted by arranging a number of gas chambers 35 with a capacity required for sending one bubble-shaped smoke in accordance with the each smoke injection needle 32 is installed so that it may be freely

reciprocated in an arrow direction by a driving gear which is not shown in the figure. In each gas chamber 35 in the movable valve 34, a supply through hole 38 being connected and disconnected to and from an individual flow passage 37 from a distributor 36 being connected to the smoke supply pipe 33 by the movement of said movable valve 34 and an injection through hole 40 being connected and disconnected to and from an injection flow passage 39 connected to the smoke injection needle 32 by the movement of the movable valve 34 are installed. The above-mentioned individual flow passage 37 and supply through hole 38 are connected when the movable valve 34 is positioned at one moving end (left end) and disconnected when it is positioned at the other moving end as shown in Figure 2. Also, the injection flow passage 39 and the injection through hole 40 being connected to the smoke injection needle 32 are /15 disconnected when the movable valve 34 is positioned at one moving end and the above-mentioned individual flow passage 37 and supply through hole 38 are connected. On the contrary, they are connected when the individual flow passage 37 and the supply through hole 38 are disconnected as shown in Figure 2.

[0034]

Furthermore, a driving member 41 for ascending and descending the injector body 30 by a driving gear, which is not

shown in the figure, is connected to the above-mentioned smoke injector 3. The driving member 41 is driven at a fixed distance (for example, 5 mm) in the extracting direction of the smoke injection needles 32 from the tuna meat M, intermittently, that is, each time a small amount of bubble-shaped smoke is sprayed from the tips of the smoke injection needles 32 pierced into the tuna meat, after the smoke injection needles 32 are once deeply pierced into the tuna meat M by its lower movement. As a result, as shown in Figure 4, smoke bubbles 51 are injected in a nearly equally dispersed state in the arrangement surface (horizontal surface) of the injection needles 32 an in the thickness direction of the tuna meat into passage traces 50 of the smoke injection needles 32 in the tuna meat M. Also, the smoke may be injected at the stage where the smoke injection needles 32 are pierced into the tuna meat.

[0035]

The smoke bubble 51 may be injected by reciprocating the above-mentioned movable valve 34 in an arrow direction by the driving gear. In other words, in Figure 3, in a state in which the movable valve 34 is positioned at the left end, the individual flow passage 37 and the supply through hole 38 are connected, and the pressurized smoke is filled into each gas chamber 35, if the injection flow passage 39 and the injection

through hole 40 are connected by moving said movable valve 34 up to the position shown in the figure, the smoke filled into the gas chambers 35 is sent out through the smoke injection needles 32 by the pressure. After sending out the smoke, if the movable valve 34 is returned to the left end, the individual flow passage 37 and the supply through hole 38 are reconnected, and the pressurized smoke is filled into each gas chamber 35. [0036]

Also, in order to suppress curving or bending of the above-mentioned smoke injection needles 32 when they are pierced into the tuna meat, a needle guide 43 having guide holes 44 into which each smoke injection needle 32 is inserted is installed in the above-mentioned injector body 30. The needle guide 43 is held to the injector body 30 by an elevating arm 45, and its ascending and descending drive is controlled. When the smoke injection needles 32 start to be descended by the driving member 41, as shown in Figure 2, the needle guide is positioned near the tip of the injection needles 32, and after said needle /16 guide 43 descends along with the driving member 41 and contacts with the tuna meat M, the needle guide is held in a stopped state at the position. When the smoke injection needles 32 are pulled out of the tuna meat M, the needle guide presses the tuna meat surface and suppresses the lift-up of the tuna meat along

with the smoke injection needles 32. After the part near the tip of the smoke injection needles 32 reaches the guide holes 44 of the needle guide 43, the needle guide is ascended along with the smoke injection needles 32.

[0037]

In order to automatically inject the smoke into the tuna meat, the smoke is injected into said tuna meat while intermittently transferring the tuna meat M by a conveyor being synchronized with the ascent and descent of the driving member 41. The above-mentioned injector body 30 is held in a fixed state, the mounting stand of the tuna meat is ascended and descended, and an operation relatively similar to the piercing operation of the smoke injection needles 32 into the tuna meat M of the above-mentioned driving member 41.

[0038]

Since the smoke bubbles injected at a fixed interval into the tuna meat are diffused to the periphery in the tuna meat, they can be permeated into the entire tuna meat in 20 min-2 h, preferably 30 min-1 h by an appropriate setup of the vertical and horizontal interval of the smoke injection needles 32 and the bubble injection interval of the driving member 41.

On the contrary, it is necessary for the interval of the above-mentioned smoke injection needles 32 and the interval

between the bubbles being determined by the bubble spray interval during the driving member 41 to be set to the interval at which the dispersedly injected smoke bubbles are permeated into the entire tuna meat in 20 min-2 h, preferably 30 min-1 h.

Also, since the diameter of the smoke injection needles in this smoke injector is almost within 1 mm, the traces of the injection needless do not remain in the tuna meat.

[0039]

In consideration of the circulation of frozen tunas, at least 2.5 months are required as the browning suppression period during freezing at -18°C, and in order to meet it, as mentioned above, the residual CO concentration in the tuna meat may be set to 1,500 μg/kg or more, preferably 1,800 or more. Also, it is preferable for the color of the tuna meat to be changed similarly to the change of the color of an untreated tuna meat with time after thawing, and in order to meet it, the residual CO concentration in the tuna meat may be set to 2,400 μg/kg /17 or less.

Furthermore, it is known that the browning period after thawing of an untreated tuna meat frozen at -60°C is within 12 days (12 days at maximum). The residual CO concentration within the above-mentioned 2,400 μg/kg is also the limit at which the

smoke-treated tuna meat is browned within 12 days similarly to the untreated tuna meat, and this fact is actually confirmed. [0040]

The above facts are summarized as follows.

(1) It is necessary for the browning suppression period during freezing at -18°C to be at least 2.5 months. In order to meet this condition, the lower limit value of 1,500 μg/kg exists in the residual CO concentration.

(2) It is necessary for the smoke-treated tuna meat not to be excessively fresh and not to be changed from a natural tuna meat color, and in order to meet these conditions, the upper limit value of 2,400 μg/kg exists in the residual CO concentration.

(3) The change of the color of the smoke-treated tuna meat with time after thawing is similar to the change of the color of an untreated tuna meat with time, and for this reason, browning is required by the Met processing within 12 days. The upper limit value of the residual CO concentration of 2,400 μg/kg in the above-mentioned (2) is required to meet this condition. [0041]

After the above-mentioned smoke treatment is finished, the tuna meat is transported to a place for consumption while maintaining an ordinary freezing in the vicinity of -18°C. Since the quality maintenance during freezing and transporting for

circulation over a long term and the browning prevention of the tuna meat for the browning suppression period during freezing can be achieved by an inexpensive freezing facility of about -18°C instead of an expensive very low-temperature freezing facility of -60°C, the energy is saved, and the economical efficiency is obtained.

Also, the very low-temperature freezing facility of -60°C is not currently installed in countries such as America and Europe other than Japan.

The very low-temperature freezing and transporting system of -60°C is unique to Japan and cannot be utilized in America, Europe, and other countries. If freezing and transporting of -18°C can be realized by the present invention, said freezing and transporting system can be utilized in the world.

[0042]

In the above-mentioned treatment method for storing a /18 tuna, if necessary, it is necessary to measure the residual CO concentration in the tuna meat. Its measuring method is limited to the A method of the Ministry of Health and Welfare in Japan, however said A method is not necessarily an appropriate measuring method. The Kumazawa method being explained by Figure 5 should be adopted. This will be explained below. Also, all

the residual CO concentrations in this specification show values being measured by the Kumazawa method.

[0043]

In the above-mentioned A method, first, water at an amount of twice is added to 300 g sample and homogenized for 1 min under an ice cooling by using a homogenizer, so that a sample solution was formed. Then, 200 g of the sample solution was transferred to a centrifuge tube and centrifuged at 10°C, and the supernatant fluid is adopted as a sample solution. Next, 50 mL of the sample solution is transferred to a head base bottle, and 5 drops of octyl alcohol as a defoaming agent, 5 mL water, and 20 mL 20% sulfuric acid were added. A lid with a silicone rubber septum was put on the bottle and heavily shaken for 2 min. After holding for 10 min, the bottle was re-shaken for 1 min, and the gas phase in the bottle was immediately sampled by a gastight syringe and poured into a gas chromatograph, and the CO concentration in the sample was attained by a separately prepared calibration curve.

On the other hand, in a method for measuring the CO concentration known as the B method, 1.5 mL clean air is transferred to the gastight syringe and poured into a vacuum pack for packing fresh fishes, 1.0 mL gas is immediately sampled

as it is, and the amount of CO is quantified by a gas chromatography.

[0044]

Next, the measurement principles of the above-mentioned A method and B method are compared, and the problems of the A method are explained.

The affinity of CO to the reducing Mb in the tuna meat is much greater than the affinity of O_2, and the coordination of O_2 is considerably suppressed. For this reason, CO reduces the amount of oxymyoglobin (O_2Mb) for coordinating O_2, so that the amount of brown Met myoglobin (MetMb) being generated is reduced. In other words, if CO is coordinated with Mb in advance, the apparent browning can be suppressed.

The coordination reaction of CO to Mb in the tuna meat is expressed as follows.

$$CO + Mb = COMb \qquad (a)$$

The higher the temperature, the smaller the equilibrium constant (stability constant) of the coordination reaction. Also, it /19 is 100 times or more greater than the equilibrium constant of a similar coordination reaction of O_2 and Mb.

$$O_2 + Mb = O_2Mb \qquad (b)$$

[0045]

For this reason, for the COMb once generated in the tuna meat, if the tuna meat contacts with the air containing little, the above-mentioned reaction (a) advances to the left and dissipates CO into the air. This fact is considered as a main cause for scattering of 14 times or more in the values of the residual CO concentration measured by the A method in measurement examples which will be mentioned later.

On the other hand, in the measurement principle of the B method, if the COMb once generated in the tuna meat contacts with the air containing little CO, the above-mentioned reaction (a) advances to the left and dissipates CO into the air. It can be said that the main cause for a critical measurement error of the residual CO concentration of the A method is utilized. In other words, the B method implicitly recognizes the defect of the A method, and both of them are self-contradictory methods. [0046]

Also, in the measurement of the residual CO concentration by the A method, it is indicated that there is a bias in the measured values in accordance with the inspection agencies designated by the Ministry of Health and Welfare, the error of the measured values is large, and there is a problem in the reproducibility.

Accordingly, 12 uniform samples were prepared from the same sample (smoke-treated bigeye tuna), and three samples (A, B, C) among them were sent to three inspection agencies (X, Y, Z) designated by the Ministry of Health and Welfare while changing the date and time, and the measurement of the residual CO concentration of the A method was requested. The residual CO concentration of these nine samples should show close values if the measuring method is valid. Also, for the rest three samples, the residual CO concentration was measured by the following Kumazawa method.

[0047]

The method for measuring the residual CO concentration developed by Mr. Hidehiro Kumazawa (professor, Faculty of engineering, Toyama University) is outlined as follows. CO coordinated in a tuna meat is dissipated into a gas phase by heating said tuna meat in a fixed amount of boiled water, and a pickup gas is blown into the boiled water. These gases are housed in a tetra bag, and the CO concentration of the gas in said bag is measured by a detecting tube or a gas chromatography.

[0048]

This Kumazawa method is explained in further detail by Figure 5. /20

(1) Water in a flask 61 with a volume of 1 L is boiled by a heater 60. The vapor being vaporized is condensed by a condenser 62 connected to the flask. The condensed water is returned to the flask 61. Glass beads 63 for expanding the electrothermal area are filled into the condenser 62, if necessary.

(2) A prescribed amount (for example, 100 g) of tuna meat 65 is immediately charged into the boiling water of the flask 61 from a sample charge port 64. At that time, the tuna meat is finely cut so that CO may be easily dissipated.

[0049]

(3) From a nitrogen bomb, a nitrogen gas as a pickup gas is blown at a fixed amount of flow (for example, 1 cm^3/s) into the boiling water through a stainless fine pipe 6. Thus, the dissipation of CO removed from the tuna meat 65 into the gas phase and the movement to tetra bags 67 for recovering gases are facilitated.

(4) In order to collect the total amount of dissipated CO diluted with the nitrogen of the pickup gas, the space from the flask 61 to the tetra bags 67 for recovering gases is held in a closed system from the moment when the tuna meat is charged into the boiling water. When the tuna meat being charged is 10 g, if

the amount of pickup gas flows is held at 1 cm^3/s, 2 L is usually sufficient as the capacity of the tetra bag.

Also, as shown in the figure, several tetra bags 67 are connected via cocks 68, and the flask 61 is always connected to one tetra bag 67 by the cock 68. When one bag is filled with the pickup gas, the tetra bag is switched to another tetra bag 67 by the operation of the cock 68, and this operation is preferably repeated until CO is not detected.

(5) The CO concentration in the tetra bags 67 is measured by a detecting tube or a gas chromatography.

[0050]

The measurement results of the above-mentioned three inspection agencies and the Kumazawa method are shown as the CO weight being included per 1 kg tuna in Table II. The value before "/" in the table shows the concentration on the 0^{th} day, and the value after that shows the concentration on the second day.

[0051]

/21

(Table II)

Inspection agency	Sample A	Sample B	Sample C
X	75/120	1100/980	1000/940
Y	270/280	350/420	600/540

Z	640/470	571/607	352/364
Toyama University (Kumazawa method)	D 1490/1310 G 1430/1180	D 1480/1240 G 1470/1220	D 1220/1040 G 1200/1050

Unit of numerical values: [μg/kg]

D: CO concentration measured by the detecting tube

G: CO concentration measured by the gas chromatography

[0052]

According to Table II, there is a large scattering of 14 times or more from 75 μg/kg at minimum to 1,100 μg/kg at maximum in the values measured by three inspection agencies based on the A method. The scattering of this measuring method largely exceeds a recognizable range as an analysis method and hints that there is an apparent problem in the reproducibility of the measurement based on the A method. On the contrary, scattering of the measurement results based on the Kumazawa method is small, and it is apparent that the reliability is high.

Also, compared with the Kumazawa method, the measured values of the A method are as small as 1/6-1/4, and the scattering is very large. The reason for this is considered that there are a number of portions having problems in the sequence of the A method. In particular, this fact agrees with the estimation in which CO is not reliably sampled (the

dissipation cannot be avoided) at the stage until the sample being injected into the gas chromatography is prepared. [0053]

Also, for the above-mentioned A method, the following /22 error generation causes can be indicated. First, at the stage where the sample solution is prepared using the homogenizer, it is assumed that the entire CO is confined in the sample solution, however at that time, CO coordinated into the tuna meat cannot be avoided from being dissipated into the gas phase. If the tuna meat coordinated with CO is brought into contact with the air, CO is dissipated into the gas phase. This is also the measurement principle of the B method.

Also, the supernatant fluid is adopted as a sample solution at the centrifugal separation stage, however at that time, it is necessary to transfer the entire CO to the supernatant fluid. However, since the solubility of CO in the aqueous solution is very small, it is doubtful that the entire CO is dissolved in the supernatant fluid. The undissolved CO escapes into the gas phase.

Furthermore, at the stage where the sample being injected into the gas chromatograph, it is also assumed that the entire CO moves to the gas phase, however at least CO with a

concentration equilibrated with CO in the gas phase also remains in the solution phase.

[0054]

There is a large scattering in the measured values due to these causes, and it is difficult to say that attaining the residual CO concentration in the tuna meat by the measurement based on the A method having no reproducibility is appropriate in the present invention in which the CO concentration is specified. For this reason, as the CO concentration in the present invention, the value measured by the above-mentioned Kumazawa method is used.

[0055]

(Effects of the invention)

As mentioned above in detail, according to the treatment method for storing a tuna of the present invention, while holding a tuna meat in a substantially raw state, antisepsis and sterilization effects are given, and the degradation and change of each component in the tuna meat can be sufficiently suppressed, even at a freezing temperature of -18°C, so that the qualities can be maintained during freezing and transporting for circulation over a long term. At the same time, browning of the tuna meat is prevented for a browning suppression period during freezing, and the color of the tuna meat is changed similarly to

the change of the color of an untreated tuna meat with time after thawing.

4. Brief description of the figures

Figure 1 shows a smoke generation mechanism being used in generating a smoke with desired components in the method of the present invention. /23

Figure 2 is a cross section showing the constitution of a smoke injector being used in the application of the present invention.

Figure 3 is a bottom view showing an arrangement state of smoke injection needles in said smoke injector.

Figure 4 is an illustrative diagram showing an injection state of smoke bubbles into a tuna meat by the smoke injection needles.

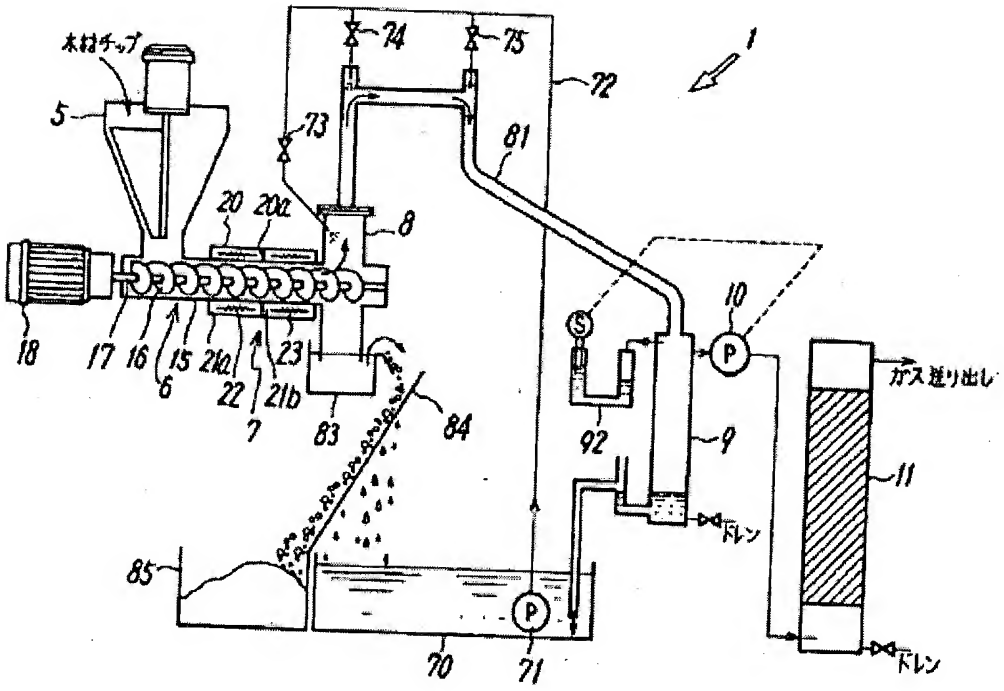
Figure 5 is a constitutional diagram showing the outlined of an apparatus for measuring the residual CO concentration in a tuna meat by the Kumazawa method.

Explanation of symbols:

M Tuna meat

50 Passage trace of smoke injection needles 32

51 Bubble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74
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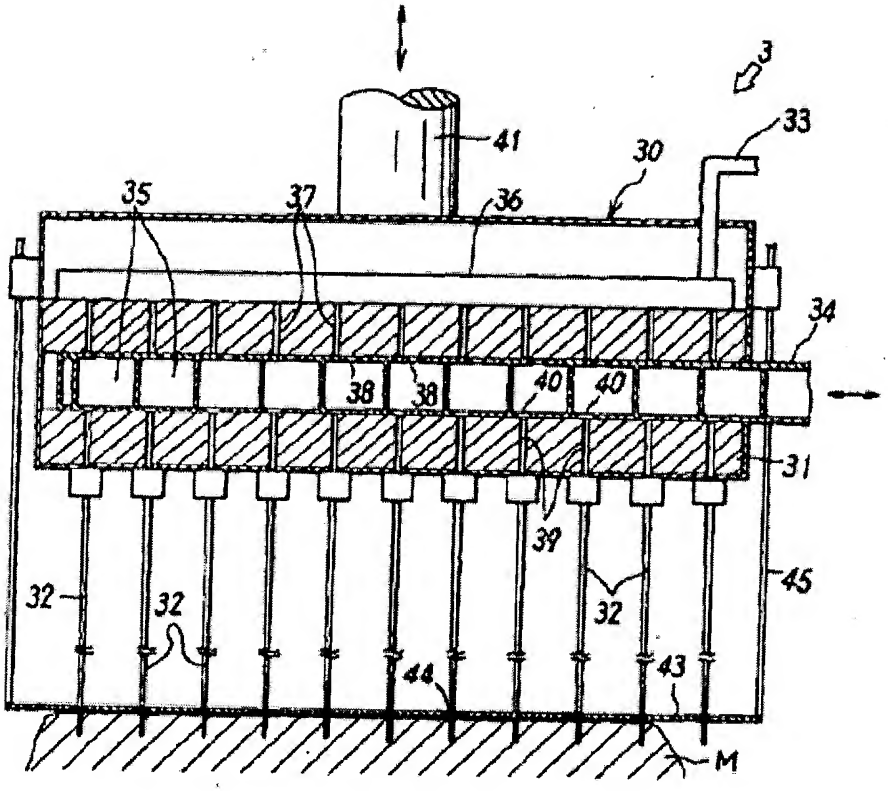
72
1
73
81
20
20a
8
10
18
17
16
15
6
21a
22
7
21b
23
83
84
92
9
11
ガス送り出し
ドレン
85
70
71
ドレン

【図２】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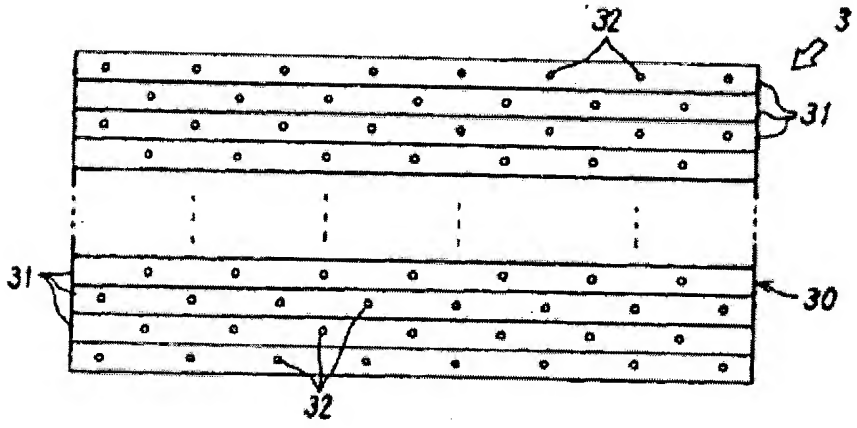
43
M

【図３】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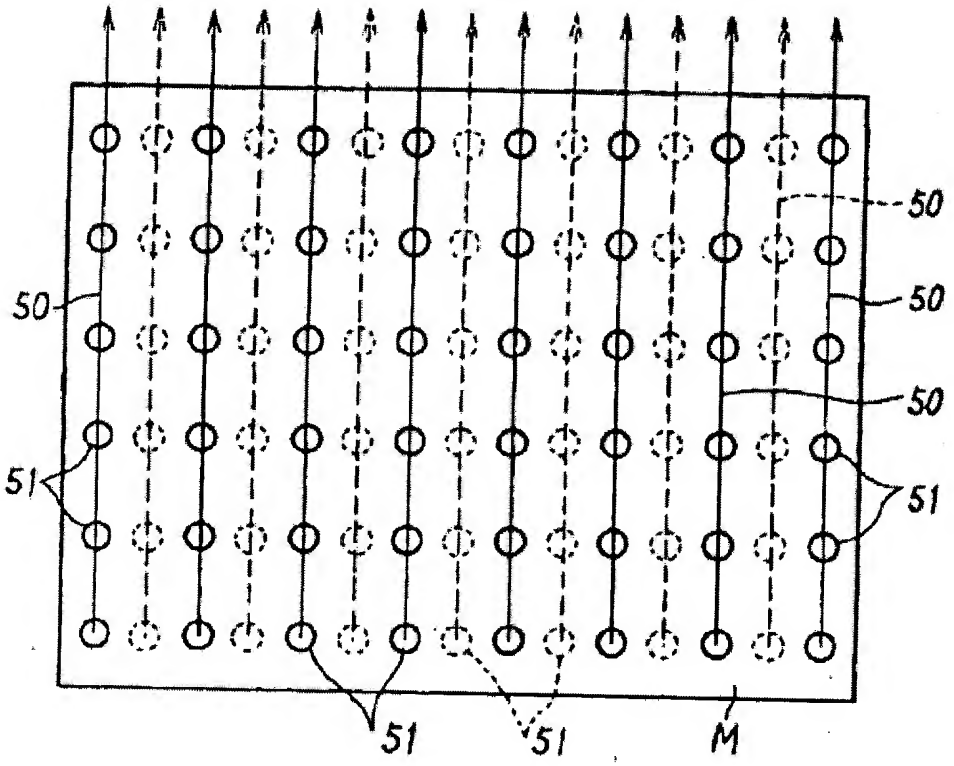
3
31
31
30
32

【図４】



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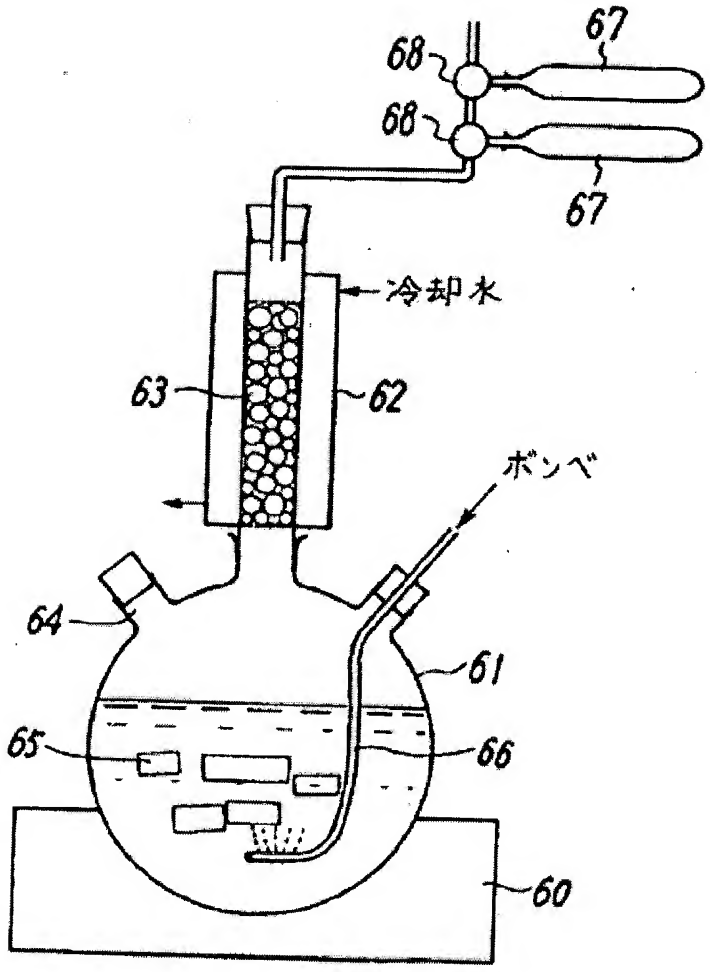

Figure 1:

1. Wood chip
2. Gas feed-out
3. Drain
4. Drain

Figure 5:

1. Coolant

2. Bomb